



Short communication

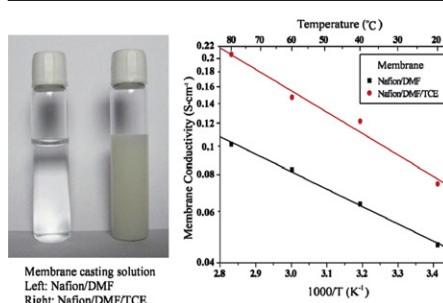
Enhanced performance of a Nafion membrane through ionomer self-organization in the casting solution

Shi-Xiong Zhao^{a,b}, Li-Juan Zhang^{a,b}, Yu-Xin Wang^{a,b,*}^aSchool of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin 300072, PR China^bTianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin 300072, PR China

HIGHLIGHTS

- Nonsolvent tetrachloroethylene leads to self-organization of ionomer in casting solution.
- Such casting solution results in Nafion membranes with greatly improved proton conductivity.
- Higher water content and water permeability of the membrane were also observed.
- The membranes were mechanically robust despite of polymer aggregation in casting solution.
- Larger clusters of sulfonate groups in the membranes were detected via SAXS and TEM.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 11 August 2012

Received in revised form

7 January 2013

Accepted 10 January 2013

Available online 29 January 2013

Keywords:

Proton exchange membrane

Nafion

Conductivity

Solution casting

Self-organization

ABSTRACT

A Nafion membrane with enhanced performance has been prepared by using a novel casting solution containing low-polarity nonsolvent tetrachloroethylene (TCE). TCE induces self-organization of the ionomer and turns the originally transparent Nafion in dimethylformamide (DMF) solution into opaque. The Nafion membrane cast from such opaque solution remains mechanically robust and shows a proton conductivity of 0.07 S cm^{-1} at room temperature, and 0.21 S cm^{-1} at 80°C under saturated humidity, which is an increase of 62% and 103% respectively over the membrane without TCE involvement. Besides, water content and water permeability of the new membrane become higher. The enhanced membrane performance is attributed to larger clusters of sulfonate groups in Nafion, which is revealed by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are considered to be a very promising alternative power source for a wide

spectrum of applications. The PEM in such fuel cells is often a performance-limiting component. Perfluorosulfonic acid membranes with the trade name Nafion are the most commonly used electrolyte in PEM fuel cells, because of their high proton conductivity as well as high thermal and chemical stability. Although the Nation has become the PEM of choice since the late-1960's and is still among the best available, it is not satisfactory in many aspects, including ohmic losses at high current density, fuel crossover when fueled with alcohols, resistance to water transport from cathode to

* Corresponding author. School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Tianjin University, Tianjin 300072, PR China. Tel./fax: +86 22 27890515.

E-mail address: yxwang@tju.edu.cn (Y.-X. Wang).

anode, proton conductance deterioration at high temperature or low humidity, and so on [1]. Therefore, numerous efforts have been made to improve the performance of Nafion membranes. One commonly adopted strategy for that purpose is to combine Nafion polymer with other materials, e.g. Other polymers or inorganic particles [2,3]. While the strategy is easy to implement and sometimes very successful, it often leads to situations that one goal is achieved at the sacrifice of others.

To avoid the above mentioned situations, other methods for making better Nafion membranes have been explored. Zhang et al. [4] added to the casting solution a “molecular gelator”, dimethylbenzaldehyde (DMBA), to promote the crystallization of membrane. The resultant Nafion membrane showed an 18% increase in proton conductivity, besides a 42% increase in crystallinity and a 32% increase in yield strength. The fuel cell with the crystallization intensified membrane also showed a 17% increase in peak power density. Lin et al. [5] exerted an electric field of 7.5 kV cm⁻¹ on a recast Nafion membrane at 120 °C for 30 min. Proton conductivity of the post-treated membrane increased by around 30% at 75 °C, 95% RH, which was attributed to the alignment of fibril-like perfluorocarbon backbone structures. Cai et al. [6] treated a commercial Nafion 212 membrane with supercritical carbon dioxide to re-organize its microstructure. The post-treated membrane presented not only higher proton conductivity but also better capability to resist methanol crossover. Lu et al. [7] prepared mesoporous Nafion membranes by adding a non-ionic block copolymer surfactant in the casting solution. The surfactant acted as a soft template, which was later removed from the membranes by refluxing with hot water. Such meso-Nafion membranes showed a much higher capability to retain water, which resulted in more than doubled fuel cell power output at 120 °C, 10% RH in comparison with Nafion 115 membrane.

In this communication, we report a novel solution casting method to obtain high performance Nafion membranes. Besides Nafion ionomer and solvent DMF, our casting solution contains also a low-polarity nonsolvent TCE, which induces intense ionomer self-organization in the casting solution. Used widely in dry-cleaning, TCE is cheap and easily available. It evaporates with the drying of the membrane, therefore no additional process for TCE removal is needed. The membrane's proton conductivity, water content, water permeability, and mechanical strength will be presented, and comparisons with conventional recast Nafion membrane will be made.

2. Experimental

2.1. Membrane preparation

Aqueous Nafion solution (5 wt. %, DE520) was purchased from Shanghai Hesen Electric Co., Ltd. The received Nafion solution was heated in a vacuum oven at 60 °C to obtain a dry Nafion resin, which was then redissolved in DMF under agitation to get a 10 wt. % Nafion/DMF solution. TCE was mixed with the solution under agitation to obtain an opaque 3 wt. % Nafion casting solution. A membrane was obtained by casting the opaque solution on a glass plate at 80 °C for 12 h, and then at 100 °C for 4 h. The membrane thus prepared will be referred to as Nafion/DMF/TCE membrane hereafter. Conventional recast Nafion membrane casts with a 10 wt. % Nafion/DMF solution was also prepared under the same condition, which will be referred to as Nafion/DMF membrane. The membranes were peeled off from glass plates in deionized water, then protonated by treating with 1 mol dm⁻³ sulfuric acid at room temperature for 24 h and rinsed thoroughly with deionized water. The thickness of the membranes in dry form is 70 µm approximately.

2.2. Membrane testing and characterization

The proton conductivity of the membranes was measured under saturated humidity using an electrochemical workstation (PARSTAT 2273, Princeton) connected to a home-made testing cell [8], where a strip of 5 mm in width cut from the membrane was pressed by two parallel stainless steel electrodes positioned 10 mm apart. The cell's temperature was controlled by a thermoregulator. The impedance spectra of membranes were obtained by sweeping from 2 MHz to 10 Hz with perturbation amplitude of 10 mV. The conductivity, σ , was calculated from the impedance data using the relation $\sigma = l/(R \cdot S)$, where l and S are the distance between the electrodes and the cross-section area of the strip, respectively, and resistance R was derived from the intersection of the characteristic spike and Re(z)-axis in Nyquist plot.

The water permeability of the membranes was measured by a diaphragm cell method [9]. The cell's compartment I and II were separated by the membrane and were filled initially with PEG400 and an aqueous solution of glucose, respectively. As water diffusing from II to I, the change of glucose concentration in II was monitored by a differential refractometer (LCD201, WINOPAL). Since water diffuses much faster than PEG400 and glucose do, it can be assumed that the detected change in II is caused dominantly by water permeation. Therefore, the water permeability was calculated based on the variation of glucose concentration with time.

The water content, i.e. the weight percentage of water in a wet membrane, was calculated from the membrane's weight in the dry and wet state. The mechanical strength of membranes was measured at room temperature using an electronic universal testing machine (WD-10D, Changchun Second Tester Factory). The sample preparation and measurement procedure were chosen in accordance with the Chinese Standard GB-13022-91.

The SAXS measurements were conducted using an X-ray diffractometer (Rigaku D/Max-2500V-PC, Rigaku) with a Cu K α source at 40 kV, 200 mA. The samples of membrane were immersed in deionized water for a week before testing to ensure full hydration. The same instrument was also used to obtain XRD data, from which the crystallinity of membrane was obtained by first identifying the crystalline (at $2\theta = 14.5^\circ$) and amorphous (at $2\theta = 16.5^\circ$ and 39.7°) peaks, and then calculating the ratio of the crystalline peak area to the sum of the three peak areas. The microscopic images of the membranes were obtained using a TEM (JEM-2100, JEOL). The samples for TEM analysis were prepared by immersing them in 1 mol dm⁻³ Pb(NO₃)₂ solution to stain the ionic domains, followed by drying, immobilizing with epoxy resin, and slicing into 50–70 nm in thickness via an ultramicrotome (Leica EM UC7) at room temperature.

3. Results and discussion

Nafion/DMF/TCE membrane shows a 103% increase in proton conductivity at the usual PEM fuel cell working temperature 80 °C, as compared with Nafion/DMF membrane (Fig. 1). It also exhibits a noticeable increase in water content and water permeability (Table 1). As fuel cells exceeding 2 A cm⁻² in current density is becoming common nowadays, the more than doubled conductivity would mean a substantial gain on power output. Meanwhile, the increased membrane water permeability would be beneficial to the water management of fuel cells. The water accumulated at the cathode owing to cathodic reaction and electroosmotic drag would diffuse to the anode side of the membrane more easily, lowering the tendency of water flooding in the cathode and membrane drying on the anode side. This is especially desirable for PEM fuel cells working at high current density.

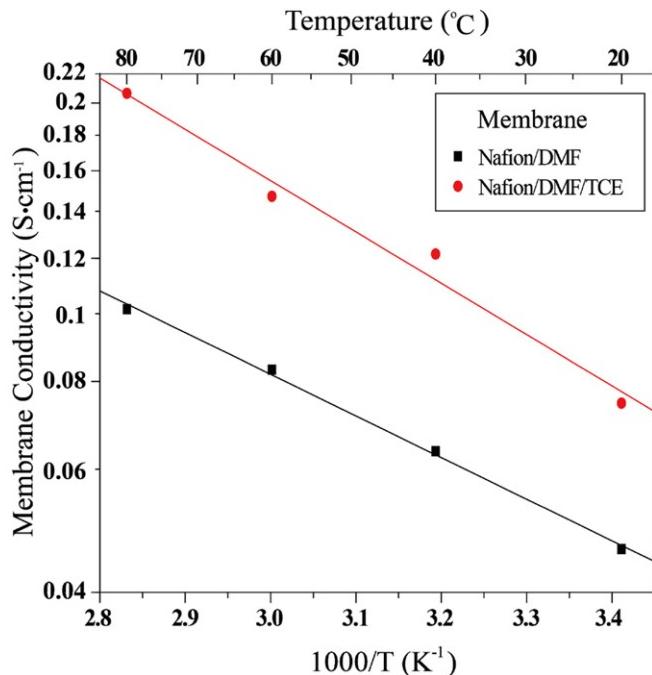


Fig. 1. Proton conductivity of the Nafion/DMF/TCE membrane and Nafion/DMF membrane under saturated humidity.

The enhanced performance of Nafion/DMF/TCE membrane arises from the addition of TCE in the casting solution. As the mixing of TCE and DMF decreases the mean polarity of the mixture, the ionomer molecules are forced to rearrange themselves through self-organization to approach their energy favorable state [10]. Both TCE and DMBA induce the self-organization of Nafion ionomer and lead to improved membrane conductivity, but the two work in different ways. Unlike DMBA which increases crystallinity in Nafion membrane [4], TCE results in lower crystallinity in Nafion/DMF/TCE membrane (Table 1).

The SAXS (Fig. 2) data clearly show the shifting of ionomer peak from Nafion/DMF membrane's around 0.3 \AA^{-1} to Nafion/DMF/TCE membrane's around 0.2 \AA^{-1} , while the origins of the broad peak around 0.4 \AA^{-1} and the spike on top of the ionomer peak at 0.3 \AA^{-1} are not clear. The shifting leads to larger Bragg distance in the case of Nafion/DMF/TCE membrane, which indicates a higher degree of phase separation. Nafion/DMF/TCE membrane also exhibits higher equilibrium water content (Table 1), therefore the size of its hydrophilic phase, consisting of ionogenic groups and absorbed water, should be larger too. This is supported by the TEM evidence in Fig. 3, which reveal that Nafion/DMF/TCE membrane has more obvious phase separation and markedly larger clusters of ionogenic groups in dry state. Because of the observed larger ionic clusters in dry Nafion/DMF/TCE membrane, its higher degree of phase separation at fully hydrated stated should not be attributed to its higher water content. Instead, the higher degree of phase separation and water content in fully hydrated Nafion/DMF/TCE membrane should originate from the larger clusters of ionogenic groups therein.

Table 1

A summary of measured properties of Nafion/DMF/TCE and Nafion/DMF membranes.

Membrane	Crystallinity %	Tensile strength MPa	Water content at 80 °C %	Water permeability cm ² s ⁻¹
Nafion/DMF/TCE	18.0	8.3	34.4	2.63×10^{-6}
Nafion/DMF	21.3	9.2	25.6	2.19×10^{-6}

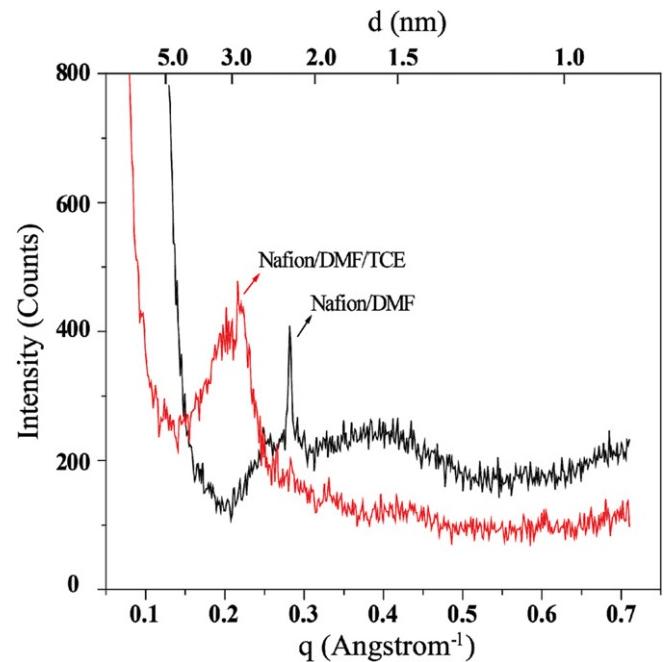


Fig. 2. SAXS curves of the Nafion/DMF/TCE membrane and Nafion/DMF membrane.

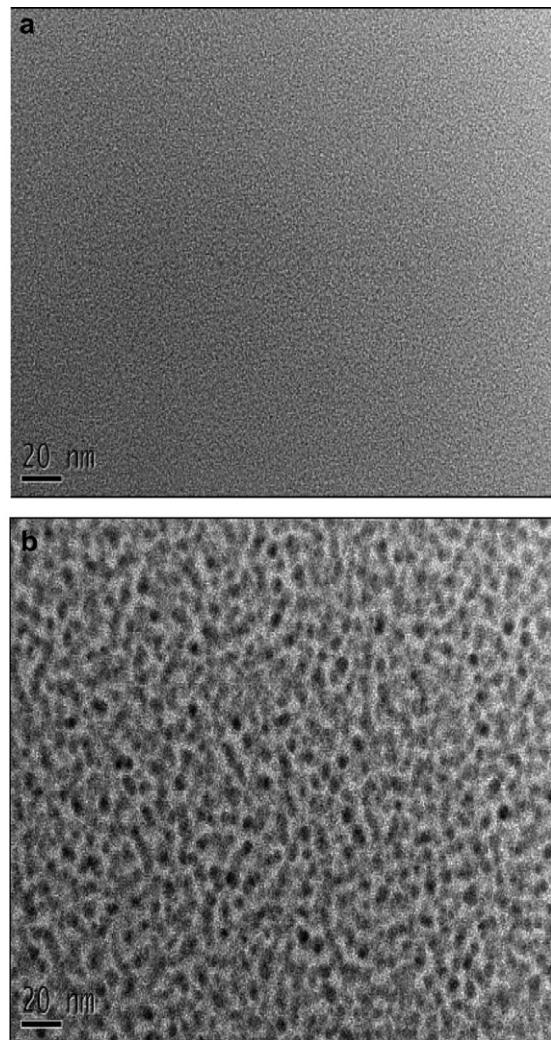


Fig. 3. TEM images of a) Nafion/DMF membrane and b) Nafion/DMF/TCE membrane.

The large clusters of ionogenic groups in Nafion/DMF/TCE membrane correlate with the high degree of ionomer aggregation in the casting solution, which suggests that a kind of membrane pre-construction takes place before solvent evaporation. Similar correlations between the ionomer arrangement in different casting solutions and that in corresponding membranes were previously observed [4,11,12]. The clusters of ionogenic groups, together with absorbed water, constitute the channels for proton and water transport. Larger clusters would mean shorter paths and lower hindrance in the transport channels, and consequently higher proton conductivity and water permeability.

Possessing a tensile strength of 8.3 MPa (Table 1), Nafion/DMF/TCE membrane can be regarded as rather robust amongst various functional polymer membranes. But this appears to be inconsistent with the common experience that casting with poor solvents would result in fragile membranes. The DMF/TCE mixture should be so poor a solvent for Nafion ionomer that the casting solution becomes opaque because of the strong light scattering by large ionomer aggregates, consequently a low strength Nafion/DMF/TCE membrane would normally be expected. Presumably, the special ionomer aggregations in the form of self-organization make the membrane exceptional.

4. Conclusion

A Nafion membrane has been prepared using a novel casting solution containing nonsolvent tetrachloroethylene. The membrane thus obtained shows a maximal 103% increase in proton conductivity and a 21% increase in water permeability, as compared with conventional recast Nafion membrane. The enhanced performance

of the membrane correlates with larger clusters of sulfonate groups, as revealed by SAXS and TEM. The membrane is mechanically robust, despite severe ionomer aggregation in the casting solution. Further study of the nonsolvent effects is underway to better understand the underlying mechanism and to further reveal its potential.

Acknowledgments

We acknowledge financial support from the Natural Science Foundation of Tianjin (11JCZDJC23800), Natural Science Foundation of China (2012BGH-0001), and the Program of Introducing Talents of Discipline to Universities (B06006).

References

- [1] S.M.J. Zaidi, *Polymer Membranes for Fuel Cells*, Springer, 2009.
- [2] B.P. Ladewig, R.B. Knott, D.J. Martin, J.C. Diniz da Costa, G.Q. Lu, *Electrochim. Commun.* 9 (2007) 781–786.
- [3] Y. Choi, D.H. Youn, S.O. Lee, Y. Kim, J.S. Lee, *Int. J. Hydrogen Energy* 37 (2012) 9766–9774.
- [4] W. Zhang, P.L. Yue, P. Gao, *Langmuir* 27 (2011) 9520–9527.
- [5] H.L. Lin, T.L. Yu, F.H. Han, *J. Polym. Res.* 13 (2006) 379–385.
- [6] L. Li, Z. Cai, L. Su, Y. Zhang, *Electrochim. Commun.* 14 (2012) 9–12.
- [7] J. Lu, H. Tang, C. Xu, *J. Mater. Chem.* 22 (2012) 5810–5819.
- [8] G. Wei, L. Xu, C. Huang, Y. Wang, *Int. J. Hydrogen Energy* 35 (2010) 7778–7783.
- [9] Q. Gao, M. Huang, Y. Wang, Y. Cai, L. Xu, *Front. Chem. Eng. China* 2 (2008) 95–101.
- [10] V. Lebedev, A. Mel'nikov, L. Vinogradova, *Polym. Sci. Ser. C* 52 (2010) 111–121.
- [11] H.L. Lin, T.L. Yu, C.H. Huang, T.L. Lin, *J. Polym. Sci. Part B Polym. Phys.* 43 (2005) 3044–3057.
- [12] C.H. Ma, T.L. Yu, H.L. Lin, Y.T. Huang, Y.L. Chen, U. Jeng, Y.H. Lai, Y.S. Sun, *Polymer* 50 (2009) 1764–1777.